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Note

## Hybridisation in Adamantane and Diamantane by the Maximum Overlap Method

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The hybridisation in adamantane and diamantane was calculated applying the method of maximum overlap. Appropriate weighting factors for different types of bonds and »double zeta« atomic functions of Clementi were used. The results are compared with NMR and X-ray diffraction measurements.

In spite of the great development of the high speed computing technique no accurate calculations on large molecules are feasible at present. Therefore, the simple semiempirical methods retain their validity, and are very useful in the description of bonding. Various kinds of maximum overlap methods belong to this class of approximate calculations. The first general method for constructing maximum overlap hybrids was given by Murrell.<sup>1</sup> This method was developed within the valence bond framework and is convenient for systems of the type  $MX_k$ . Murrell's procedure has been made more straightforward by Golebiewski<sup>2</sup>. Lykos and Schmeising<sup>3</sup> treated the construction of the maximum overlap hybrids from the molecular orbital point of view. They maximised the squares of the values of the bond overlaps reducing the whole procedure to the eigenvalue problem of the overlap matrix.

Coulson and Goodwin<sup>4</sup> performed maximum overlap calculations on the first three cycloalkanes. They found that the results were in fairly good agreement with a more elaborate valence bond treatment<sup>5</sup>. An improvement was made in this type of calculation by introducing scale factors for different bonds<sup>6</sup>. This has been widely exploited in the investigation of highly strained cyclic hydrocarbons<sup>7-9</sup>, and satisfactory results have been obtained especially when Clementi atomic orbitals were used<sup>8,9</sup>.

Here we report the maximum overlap calculations for adamantane and diamantane. Because of their unusual physical, chemical and structural properties, these molecules are of special interest for chemists<sup>12</sup>.

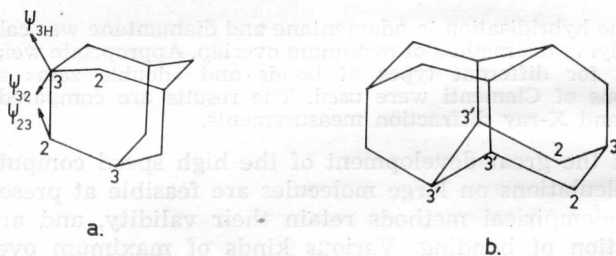
Briefly, the method applied here consists of the following<sup>6,7,9</sup>: by mixing *s* and *p* orbitals one obtains hybrids of the general form

$$\psi_{ij} = a_{ij}(s) + b_{ij}(p) \quad (1)$$

These hybrids can also be represented in the shortened  $sp^n$  form, where *n* stands for  $b_{ij}^2/a_{ij}^2$  and is not necessarily an integer. The total overlap of the molecule is

$$S = k_{CC} \sum_{C-C} S_{CC} + k_{CH} \sum_{C-H} S_{CH} \quad (2)$$

where the summation goes over all bonds.  $S_{AB}$  denotes the overlap integral  $\int \psi_A \psi_B d\tau$  of the two overlapping orbitals. The weighting factors  $k_{CC}$  and  $k_{CH}$  are introduced to compensate for the difference in bond energy between the two types of bonds. They depend on the nature of the atomic orbitals used in the calculations. We employed the »double zeta« functions of Clementi<sup>10</sup>, which gave the weighting factors<sup>9</sup>:  $k_{CC} = 121.17$  and  $k_{CH} = 135.86$ . The coefficients of the hybrids  $\psi_{ij}$  are varied until the expression (2) reaches its maximum value. Since the knowledge of the interatomic angles is not necessary in this procedure these angles were taken as additional parameters. Thus, it was possible to determine the interatomic angles theoretically. In our procedure the interatomic distances were fixed at 1.54 Å for the C—C bond and 1.07 Å for the C—H bond for both molecules. In Fig. 1. secondary and tertiary carbon

Fig. 1. a) Adamantane  $C_{10}H_{16}$ ;b) Diamantane  $C_{14}H_{20}$ .

atoms are denoted as 2 and 3 respectively. The hybrid orbital  $\psi_{ij}$  is directed from the atom  $i$  to the atom  $j$ . The hybrids which form the C—H bonds are designated  $\psi_{iH}$ . The inclination of the hybrid  $\psi_{ij}$  to the straight line joining two neighbouring atoms is denoted as  $\omega_{ij}$ . In the numerical procedure, it is more convenient to take the interhybrid angles as parameters instead of the coefficients  $a_{ij}$ <sup>6</sup>.

### Adamantane

Adamantane  $C_{10}H_{16}$ , synthesised first by Prelog and Seiwert<sup>11</sup> and later by Schleyer\*, is a tetrahedral molecule with CH groups on the vertices and  $CH_2$  groups on the edges of a tetrahedron. Its crystal and molecular structure is determined by electron and X-ray diffraction investigations<sup>13-16</sup>. All measurements have been consistent with the tetrahedral angles and with lengths of 1.54 Å and 1.09 Å for C—C and C—H bond respectively. These structural parameters are »ideal« and characterise strain free molecules. In our calculations the angle  $\angle_{323}$  was chosen as the molecular parameter and the deviations of the hybrids  $\omega_{23}$  and  $\omega_{32}$  as hybridisation parameters. The results are summarised in Table I. The deviations of the hybrids at the maximum value of the expression (2) are  $\omega_{23} = \omega_{32} = -0.8^\circ$ . This means that the hybrids are bent inside the molecule. However, we can neglect these small deviations and consider the C—C bonds to be straight.

### Diamantane

Diamantane  $C_{14}H_{20}$  (Fig. 1) is the second member of the adamantanalogous series whose three-dimensional extension is the diamond lattice. Recently an elegant synthesis of this compound has been carried out by Cupas, Schleyer and Trecker.<sup>17</sup> An X-ray investigation has been performed by Karle and Karle<sup>18</sup>. Diamantane consists of two fused adamantanes with one common cyclohexane ring. However,

\* For an excellent review on adamantane chemistry see paper by Fort and Schleyer<sup>12</sup>.

their tetrahedrons are somewhat distorted. Thus two parameters are needed to describe the molecular skeleton: the angles  $\angle_{3,3,3}$  and  $\angle_{323}$ . For the sake of simplicity the bonds in the central cyclohexane ring  $3' \dots 3'$  are supposed to be straight bonds. The hybrid deviations at maximum value of expression (2) are  $\omega_{32} = -1^\circ$ ,  $\omega_{23} = \omega_{23}' = -0.95^\circ$  and  $\omega_{3'2} = 1.35^\circ$ . The geometrical angles are in better agreement with the experimental data (Table I) than might be expected for this type of calculation. Although we cannot state that the hybridisation itself determines the geometrical angles, we can say that in this case hybridisation follows the geometry very closely.

Many physical and chemical properties can be correlated with the *s* character of the hybrids<sup>19</sup>. Our results can be compared with the available NMR data<sup>17,20</sup>. Using the Muller-Pritchard<sup>21</sup> relationship for the spin-spin coupling constant  $J_{CH} = 5 s^2\%$  one obtains 133 cps for the methylene proton, whereas the experimental value is  $120 \pm 1$  cps. This indicates a somewhat too large *s* character of the C—H hybrids. The chemical shift can be qualitatively explained by the *s* content of the hybrids, since a hybrid more rich in *s* orbital shields the proton more effectively. The NMR spectrum of adamantane<sup>20</sup> shows two chemical shifts: 1.88 ppm for the CH proton and 1.78 ppm for the CH<sub>2</sub> proton. Hybridisation itself cannot explain such a small difference, as indicated by the hybridisation ratios ( $n_{2H} = 2.8$ ,  $n_{3H} = 2.7$ ) in Table I, but according to a comparable hybridisation in the two types of C—H bonds one can expect nearly the same chemical shifts. Analogously, practically the same hybridisation state in diamantane carbon atoms ( $n_{2H} = 2.8$ ,  $n_{3H} = 2.7$ ,  $n_{3'H} = 2.8$ ) indicates similar chemical shifts. They are, in fact, identical<sup>17</sup> ( $\delta = 1.68$  ppm).

The maximum overlap method has many advantages. It is a simple, pictorial model, which corresponds to the intuitive representation of the chemical bond. However, this method has no proper theoretical foundation. Nevertheless, it is interesting to point out the apparent similarity<sup>22</sup> of the method of Golebiewski<sup>2</sup> with the LCAO—MO treatment introduced by Hall<sup>23</sup> for calculations of bond orders. If we assume that the resonance integral matrix is equal to the overlap matrix the two methods are identical. Similarly, Lykos and Schmeising<sup>3</sup> have shown that a construction of hybrids becomes equivalent to the Hückel method for  $\sigma$ -electrons, when homonuclear molecules are considered. This fact may be regarded as additional support to the validity of the maximum overlap method. When the overlap matrix nearly commutes with the Hamiltonian matrix, the results of the simple methods based on overlap and more sophisticated approaches with well defined Hamiltonians should give similar results.

Several applications of the maximum overlap method to the investigations of the strained cyclic hydrocarbons<sup>4,6-9</sup> proved that the method is useful. In the case of strainless adamantane-like molecules variations of molecular parameters between bonds and molecules are rather small and the maximum overlap method becomes too crude of an approximation. However, deviations of molecular angles from the ideal tetrahedral values are obtained in complete agreement with experimental data.

There are also some disadvantages of the maximum overlap method. For example, the ionic character of the bond is not incorporated into the scheme and promotion energy between *s* and *p* orbitals is neglected. An improvement in this respect is desirable. Finally, the hybrids obtained by the maximum

TABLE I

Maximum Overlap Hybrids, Hybridisation Ratio  $n = b_{ij}^2 / a_{ij}^2$   
Interhybrid Angles, and Molecular Angles

Hybrids	n	Bond overlap	Interhybrid angle	Geometrical angle calcd.	Geometrical angle exptl.
<i>Adamantane</i>					
$\psi_{23} = 0.4846 (s) + 0.8748 (p)$	3.26	0.6467	$\angle 323 = 107.87^\circ$	$\angle 323 = 109.47^\circ$	$109.47^\circ \pm 1.5^\circ$
$\psi_{32} = 0.4923 (s) + 0.8704 (p)$	3.13		$\angle 232 = 108.56^\circ$	$\angle 232 = 109.47^\circ$	$109.47^\circ \pm 1.5^\circ$
$\psi_{2H} = 0.5150 (s) + 0.8572 (p)$	2.77	0.7366	$\angle H2H = 111.16^\circ$	$\angle H2H = 111.16^\circ$	$109.47^{0*}$
$\psi_{3H} = 0.5225 (s) + 0.8528 (p)$	2.66	0.7394			
<i>Diamantane</i>					
$\psi_{23} = 0.4898 (s) + 0.8718 (p)$	3.17	0.6487	$\angle 323 = 108.40^\circ$	$\angle 323 = 110.25^\circ$	$110.17^\circ \pm 0.25^\circ$
$\psi_{32} = 0.4930 (s) + 0.8701 (p)$	3.11		$\angle 232 = 108.72^\circ$	$\angle 232 = 108.83^\circ$	$108.75^\circ \pm 0.25^\circ$
$\psi_{23} = \psi_{23}$	3.17	0.6484			
$\psi_{3 \cdot 2} = 0.4879 (s) + 0.8729 (p)$	3.20				
$\psi_{3 \cdot 3} = 0.4979 (s) + 0.8672 (p)$	3.03	0.6525	$\angle 3'3'3' = 109.50^\circ$	$\angle 3'3'3' = 109.50^\circ$	$108.75^\circ \pm 0.25^\circ$
$\psi_{2H} = 0.5100 (s) + 0.8602 (p)$	2.84	0.7352	$\angle H2H = 110.57^\circ$	$\angle H2H = 110.57^\circ$	
$\psi_{3H} = 0.5205 (s) + 0.8538 (p)$	2.69	0.7382			
$\psi_{3 \cdot H} = 0.5159 (s) + 0.8567 (p)$	2.76	0.7357			

\* assumed value<sup>14</sup>.

overlap procedure may be used as initial wave functions in more sophisticated calculations, and such an application has yet to be examined.

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## IZVOD

## Hibridizacija u adamantanu i dijamantanu metodom maksimalnog prekrivanja

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Izračunata je hibridizacija u adamantanu i dijamantanu primjenom metode maksimalnog prekrivanja. Pri tome su upotrijebljene Clementijeve »double zeta« atomske funkcije<sup>10</sup> i odgovarajući težinski faktori za C—C i C—H veze<sup>9</sup>. Rezultati su uspoređeni s eksperimentalnim podacima.

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